Supporting Information for manuscript entitled *"Enhanced Photocatalytic Activity of Hybrid Fe_2O_3-Pd Nanoparticulate Catalysts"* by Yanhu Wei, Shuangbing Han, David A. Walker, Scott C. Warren, Bartosz A. Grzybowski*

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Section 1. Morphologies of hybrid Fe_2O_3-Pd nanoparticles in the as-prepared sample.

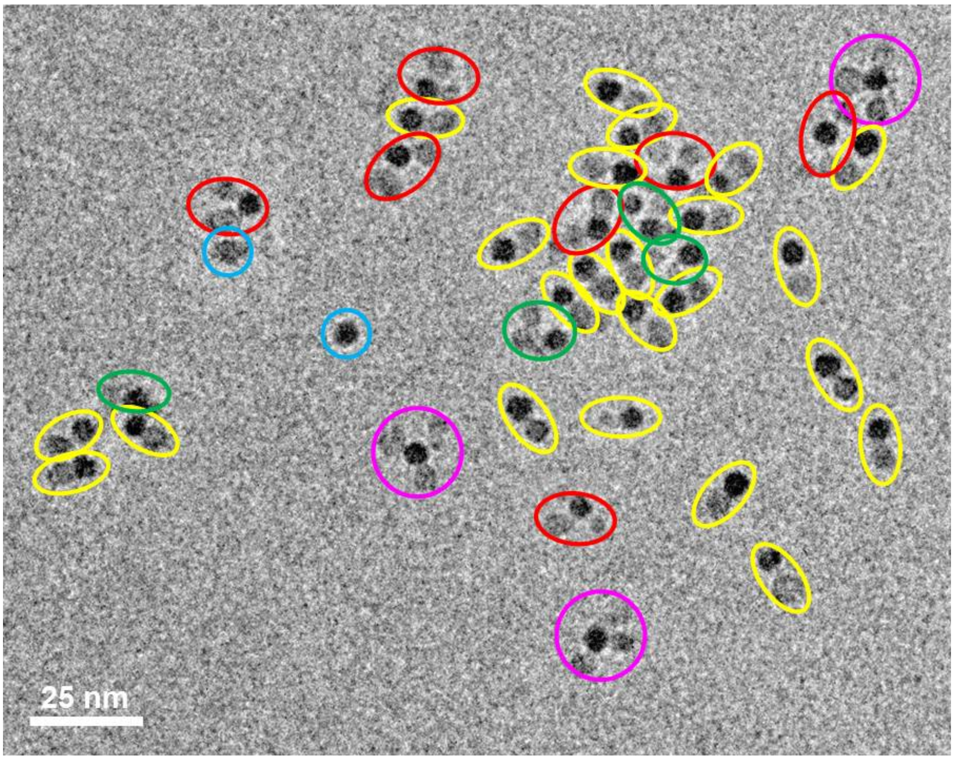

Figure S1. A typical TEM image of as-prepared Fe_2O_3-Pd nanoparticles containing hybrid dimers (circled in yellow ovals), trimers (red ovals), tetramers (violet circles), few single-component particles (blue circles) and particles that cannot be assigned unambiguously (green ovals). Within the NPs, the Fe_2O_3 domains appear grey, the Pd ones appear black.

The mixture of as-prepared Fe_2O_3-Pd nanoparticles consisted of ~91% hybrid particles (including ca. 49% dimers, 26% trimers and 16% tetramers) and ~9% single-component particles (statistics based on the analysis of ca. 300 NPs from 8 TEM images; see also Figure S1).

Section 2. The spectral characteristics of the light source used.

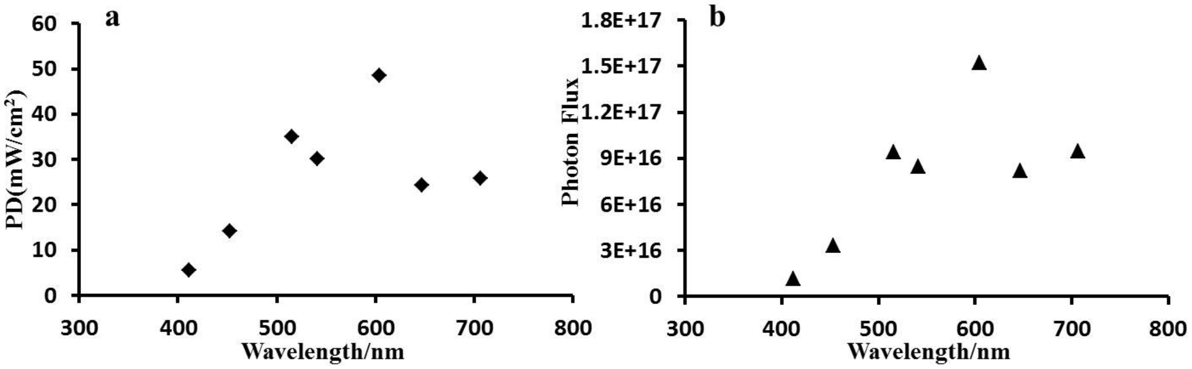

Figure S2. (**a**) The power density (mW/cm^2) and (**b**) the photon flux (photons/S/cm^2) at different wavelength (from 400 to 700 nm) of the light source used in our experiments (Edmund Optics MI-150 High-Intensity Illuminator).

Section 3. Catalytic performance of mixed Pd and Fe$_2$O$_3$ nanoparticles.

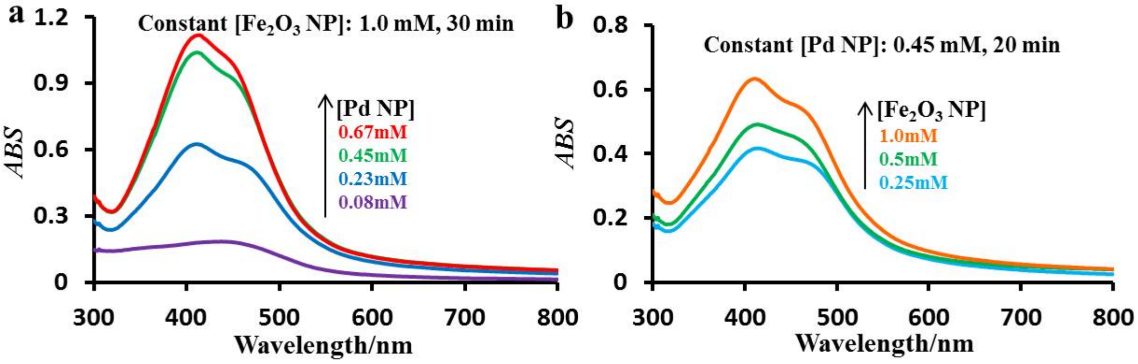

Figure S3. (**a**) The UV-Vis spectra of Ag NPs produced in the presence of different concentrations of Pd NPs (red curve: 0.67 mM, green curve: 0.45 mM, blue curve: 0.23 mM, purple curve: 0.08 mM) at constant 1.0 mM Fe_2O_3 NPs and 30 min irradiation. (**b**) The UV-Vis spectra of Ag NPs formed in the presence of different concentrations of Fe_2O_3 NPs (orange curve: 1.0 mM, green curve: 0.5 mM, light blue curve: 0.25 mM) at constant 0.45 mM Pd NPs and 20 min irradiation.

The SPR intensity of the produced Ag NPs increased with the increase of either [Pd NP] at constant [Fe_2O_3 NP] (Fig.S3a) or [Fe_2O_3 NP] at constant [Pd NP] (Fig. S3b). In the former case, increasing Pd concentration increases the probability of charge transfer from Fe_2O_3 NPs to Pd NPs (although this effect becomes less pronounced when [Pd NP] > 0.45 mM). In the latter case, the increased production of Ag NPs is due to the increase in light absorption by more Fe_2O_3 "centers" being present. We note, however, that in both cases, the efficiencies of photocatalytic production (as reflected by the intensity of the Ag NP SPR peak) remain significantly lower than those achieved with hybrid Fe_2O_3-PdNPs discussed in the main text.

Section 4. TEM images of Pd and Fe_2O_3 nanoparticles.

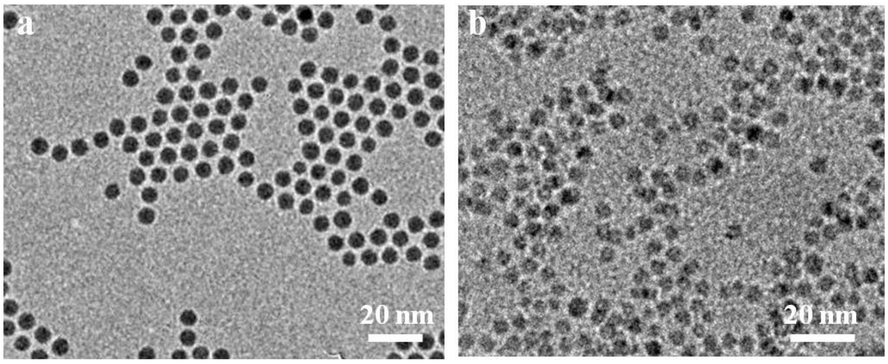

Figure S4. (a) ~5.5 nm Pd NPs and **(b)** ~5.0 nm Fe_2O_3 NPs used in control experiments.

Section 5. The UV-vis spectra of Fe_2O_3, hybrid Fe_2O_3-Pd and Pd Nanoparticles

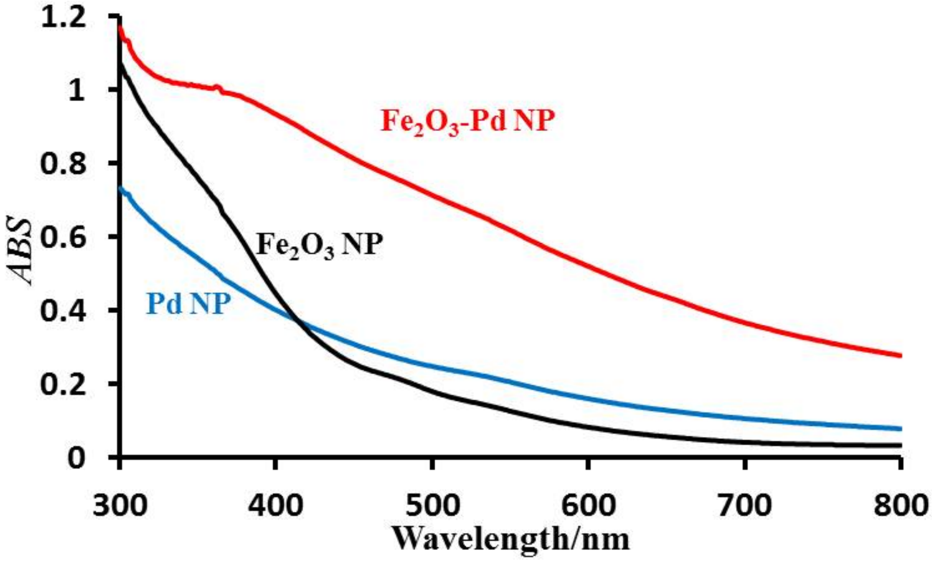

Figure S5. The UV-Vis spectra of as-prepared hybrid Fe_2O_3-Pd NPs (red curve, [Fe]=0.36 mM and [Pd]=0.14 mM), Fe_2O_3 NPs (dark curve, [Fe]=0.36 mM) and Pd NPs (blue curve, [Pd]=0.14 mM) before irradiation.

The Pd NPs show a monotonically decreasing absorption from 300 to 800 nm (blue curve), which is consistent with the reported spectra of Pd NPs for particle sizes less than 25 nm (Q. Zhang *et al. ACS Nano* **2009**, *3*, 139-148; Y. Chang *et al. J. Phys. Chem. C* **2009,** *113,* 18761-18767). The UV-Vis spectra of Fe_2O_3 NPs show intense absorption between ~320 and ~420 nm (dark curve) with an absorption coefficient that decreases with increasing wavelength to the (indirect) band gap energy of about 2.1 eV. These features agree with the reported spectra of Fe_2O_3 (P. Degen e*t al. Langmuir* **2008,** *24,* 12958-12962). The as-prepared Fe_2O_3-Pd NP hybrids have a broad and “shallow” band centered at around 380 nm with a tail extending up to 800 nm (red curve). The fact that the absorption spectrum of the hybrid NPs is not a simple sum of Pd + Fe_2O_3 spectra is an effect frequently observed in hybrid metal-semiconductor nanoparticles (Shaviv *et al. ACS Nano* **2011**, *5*, 4712-4719; J. Li *et al. Coordination Chemistry Reviews* **2009**, *253*, 3015–3041).

Section 6. Experiments with Fe_2O_3-Pd NPs in the presence and in the absence of phenol.

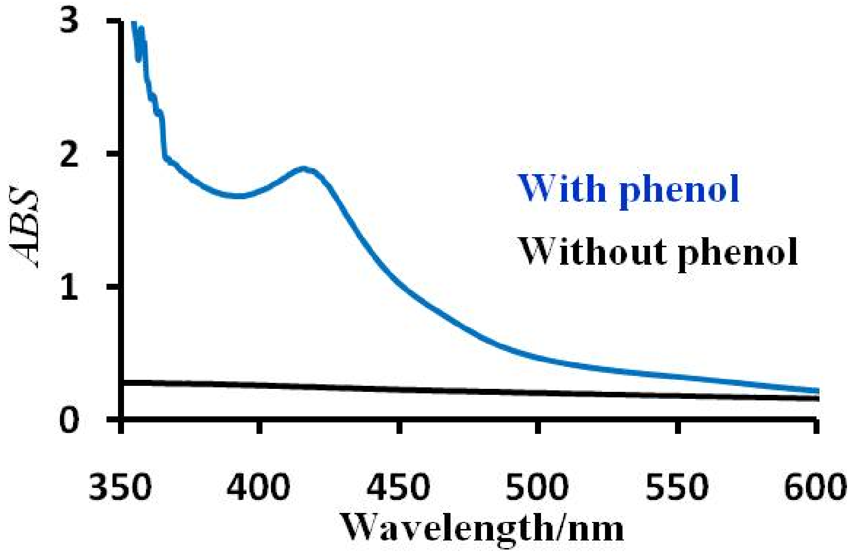

Figure S6. UV-Vis spectra recorded in the AgOAc/Fe_2O_3-Pd NP system in the presence and in the absence of phenol after 30 min irradiation.

Section 7. Dependence of Ag NP size on the irradiation time.

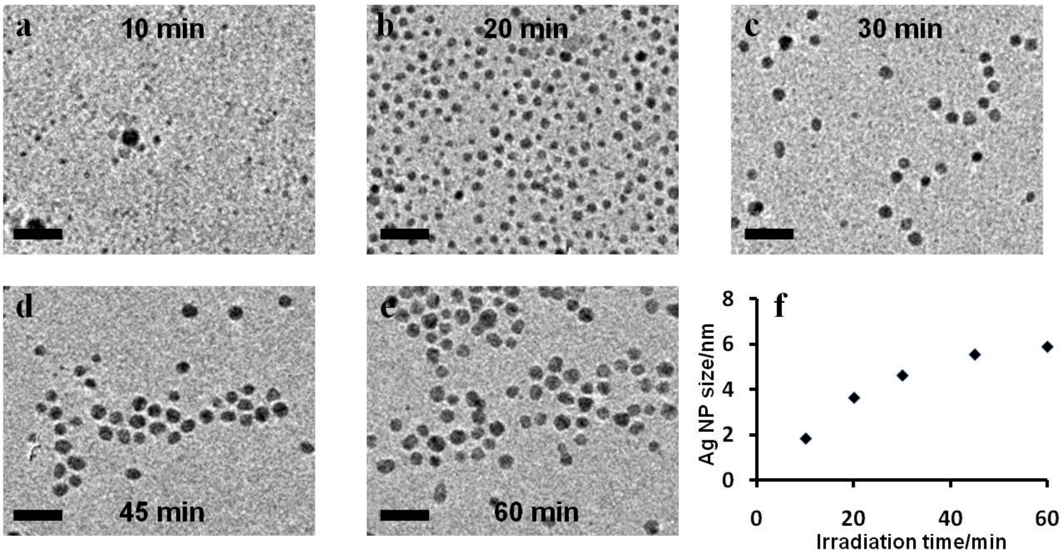

Figure S7. Dependence of Ag NP size on the irradiation time: **(a)** 10 min, **(b)** 20 min, **(c)** 30 min, **(d)** 45 min, **(e)** 60 min, **(f)** Plot of the Ag NP size vs. irradiation time. All scale bars are 20 nm. The concentration of $AgNO_3$ used is 6.25 mM.

Section 8. Dependence of Ag NP size on the concentrations of $AgNO_3$ salts

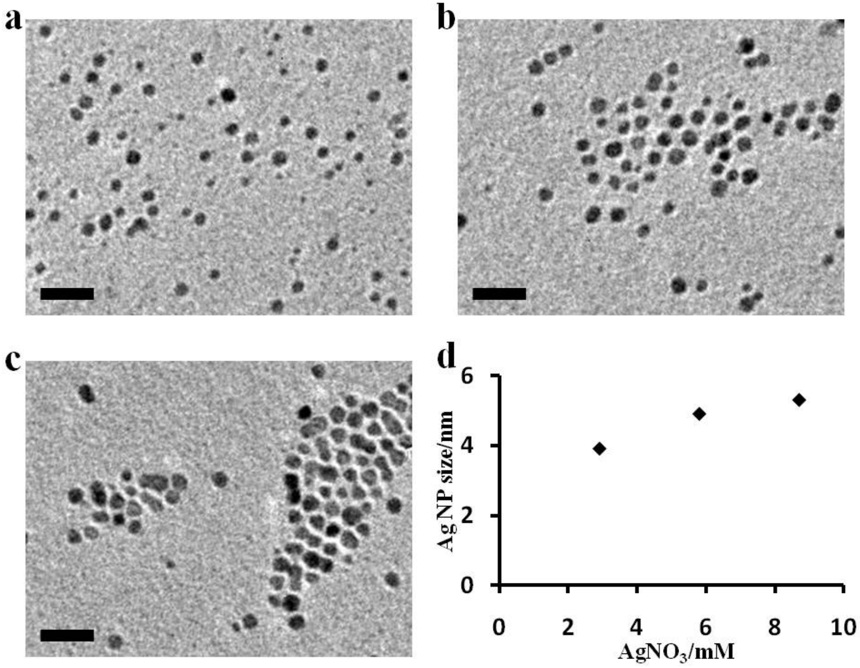

Figure S8. The dependence of Ag NP size on $AgNO_3$ concentrations: **(a)** 2.9 mM, **(b)** 5.8 mM, **(c)** 8.7 mM. Irradiation time is 30 min. All scale bars are 20 nm.

Section 9. Deposition of Ag NPs on Pd domains of hybrid particles

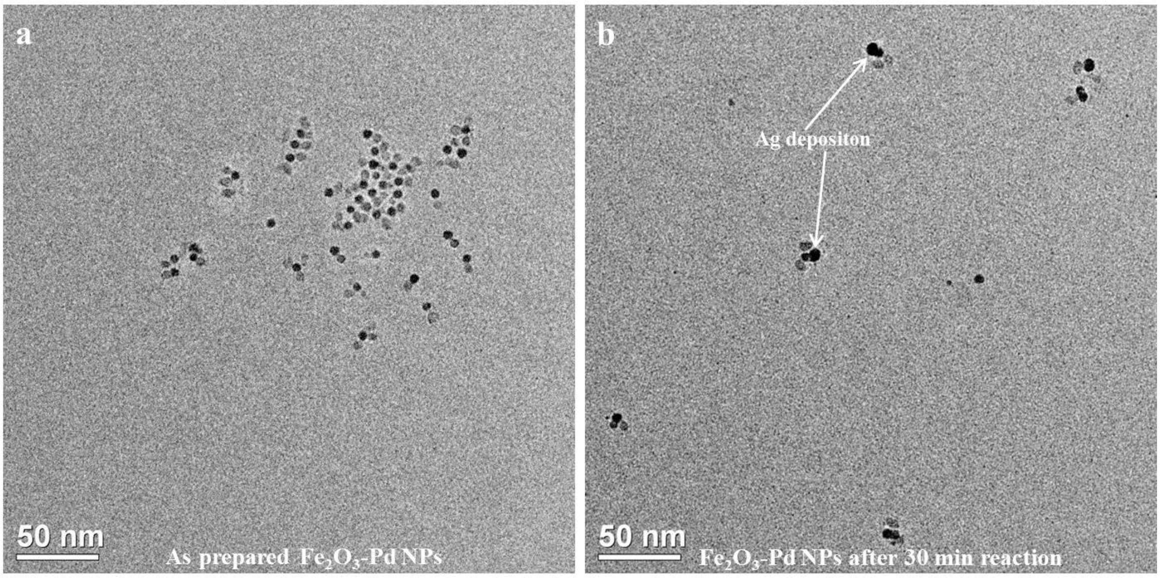

Figure S9. (**a**) A typical TEM image of as-prepared Fe_2O_3-Pd NPs (5.9 ± 0.8 nm Fe_2O_3 domain, *light grey*, and 5.5 ± 0.5 nm Pd domain, *dark*). (**b**) The TEM image taken after 30 min of irradiation. While the Fe_2O_3 domains retain their original size (~6.0 ± 0.8 nm Fe_2O_3), the Pd domains appear significantly larger (~8.5 ± 1.1 nm) due to the deposition of Ag.

During the photocatalytic reduction, we observed the deposition of Ag NPs onto Pd domains but not Fe_2O_3 domains after 30 min reaction, consistent with our hypothesis that photoexcited electrons transfer and reduce $AgNO_3$ to Ag NPs at Pd domains (Fig. S9).